

LASER RAMAN SPECTROSCOPIC MEASUREMENTS OF A DESERT-VARNISHED BASALT AND IMPLICATIONS FOR *IN-SITU* ANALYSIS OF MARTIAN ROCKS. E. J. Israel, R. E. Arvidson, A. Wang, J. D. Pasteris, and B. L. Jolliff, Dept. of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130.

Current plans for several lander and rover missions to Mars (including the recently launched Mars Pathfinder with the Sojourner rover) suggest many opportunities for the *in-situ* study of Martian rocks. In anticipation of these opportunities, we have analyzed a Martian analog sample using a laser Raman microprobe (in conjunction with petrographic and electron microprobe analysis) to demonstrate the potential usefulness of the Raman spectroscopic technique for *in-situ* analysis of Martian samples. Raman spectroscopy should be a useful technique for analyzing Martian mineralogy as it is well-suited for identifying individual species of silicates, carbonates, sulfates, and phosphates [1]. This work is a continuation of research presented at the 1996 LPSC [2].

The sample used in this research is a varnished basalt from Lunar Crater Volcanic Field, Nevada [2]. Desert varnish is a thin, discontinuous deposit of amorphous material containing primarily clays and Mn and Fe oxides and ranging in thickness from ~1 to 100 μm [3]. A photomicrograph of a thin section of the sample (Figure 1) shows the general appearance of desert varnish. The fine-grained nature, layering, and variable thickness of the varnish are all apparent. There is evidence from both Earth-based reflectance spectra [4,5,6] and from Viking Lander images [7,8,9] for the presence of fine-grained coatings on the surfaces of many Martian rocks. Although the varnish coating on this sample may not be mineralogically similar to Martian rock coatings, the importance of this analog is that it is an igneous rock with a thin, fine-grained coating.

Thin sections of the varnished rock sample were analyzed using wavelength dispersive electron-microprobe (EMP) analysis. Quantitative chemical data were obtained by probing the varnish layers with an electron beam with a spot size of approximately 5 μm . Raman spectra were acquired from thin sections and from the varnished surface of the hand sample using a laboratory Raman microprobe (S3000TM Jobin-Yvon) with an intensified diode array multichannel detector, and the 514.5 nm Ar^+ laser line as an excitation source.

Chemical analysis reveals the varnish composition to be inhomogeneous. Q-mode factor analysis performed on the electron microprobe data showed the importance of the oxides in explaining the overall chemical composition of the varnish. This analysis indicates that varnish composition is dominated by the presence of Mn-oxides, clays, and apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$). The EMP data further indicate that the Mn-oxide component of the varnish is likely a combination of pyrolusite (MnO_2) and romanechite ($\text{BaMn}^{2+}\text{Mn}^{4+}_8\text{O}_{16}(\text{OH})_4$) and that the clay component is an illite-montmorillonite mixture.

Spectra obtained with the Raman microprobe concur with the findings from the analyses of the electron microprobe data in that both Mn-oxides and apatite are indicated. The bottom spectrum in Figure 2 is that of the varnish as detected from the unprepared surface of the hand sample. The broad

band centered near 637 cm^{-1} is the most distinctive feature observed in the many varnish spectra taken from both the thin section and hand sample of the rock. The other spectra in Figure 2 are of several Mn-oxide standards. The correlation of peak position between the varnish and the various Mn-oxides indicates that an Mn-oxide or a combination of Mn-oxides is present in the varnish. Romanechite and pyrolusite are more likely than manganite because the manganite spectrum also contains a peak at 408 cm^{-1} , which is not observed in any of the varnish spectra. However, a peak at that position in the varnish spectra may be lost in the background noise, so manganite cannot be discounted completely. Because the position of the main broad band in the varnish spectra can vary between ~ 620 and 640 cm^{-1} , it is most likely that the Mn-oxide component is not a single Mn-oxide, but a combination of two or more Mn-oxides, the relative amounts of which may vary from place to place within the varnish. This is consistent with the overall heterogeneity of the varnish. An additional feature of the main varnish band is its width. The Mn-oxide standards with peak positions similar to that of the varnish show relatively sharp peaks. Only the fine-grained lithiophorite precipitate shows a much broader peak. Although the peak position of the lithiophorite peak is higher than those observed in the varnish and thus indicates that it is not present in the varnish, the width of the peak is indicative of the precipitate's fine grain size. The same inverse correlation may hold between peak width and grain size in the varnish.

The top and bottom spectra in Figure 3 were obtained from the varnished surface of the hand sample. The middle spectrum was obtained from the varnished edge of a thin section while it was propped edge-on. These configurations most closely simulated the conditions which would be encountered during a rover mission when the rough surface of the rock would be sampled directly. The bottom two spectra reveal the presence of an Mn-oxide and a Ca-phosphate phase - both indications that the varnish is detected. The top spectrum shows the characteristic peak of plagioclase - a prominent mineral in the basaltic host rock. The detection of plagioclase indicates that at this sample site the varnish is either very thin or not present, thus allowing the detection of a mineral of the host rock.

These results indicate that on Mars, there is the potential for using a laser Raman microprobe to analyze the mineralogy of both the host rocks and any coatings that may be present. If, upon examination of a coated surface, no mineral signatures are detected or the only signatures are from the coatings, it will be necessary to find a fresher surface to analyze host-rock mineralogy. This may involve looking for a fresher exposed surface that lacks coatings. Another option is to have a mechanism on the rover capable of breaking the rock open or drilling into it so that a fresh surface could be examined.

RAMAN SPECTROSCOPY OF VARNISHED BASALT: E. J. Israel, et al.

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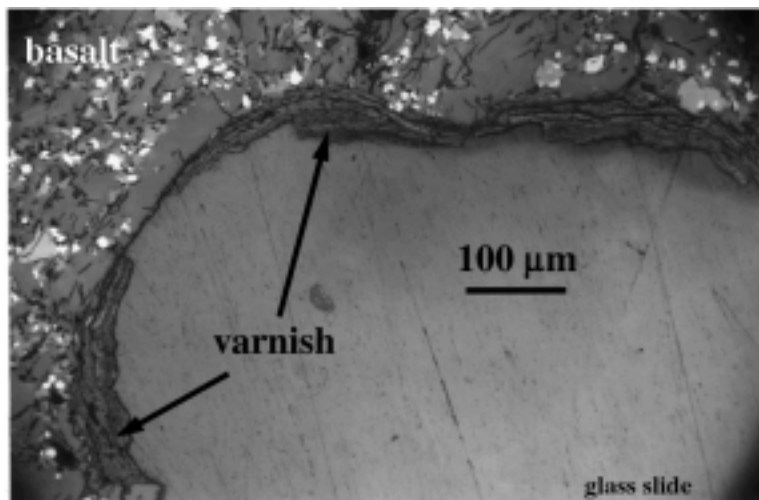


Figure 1: Photomicrograph of a thin section of the basalt sample taken under reflected light. Layering, variable thickness, and the fine-grained nature of the varnish are apparent. Thickest varnish in this region is ~60 μm . Image size = 0.82 x 0.56 mm.

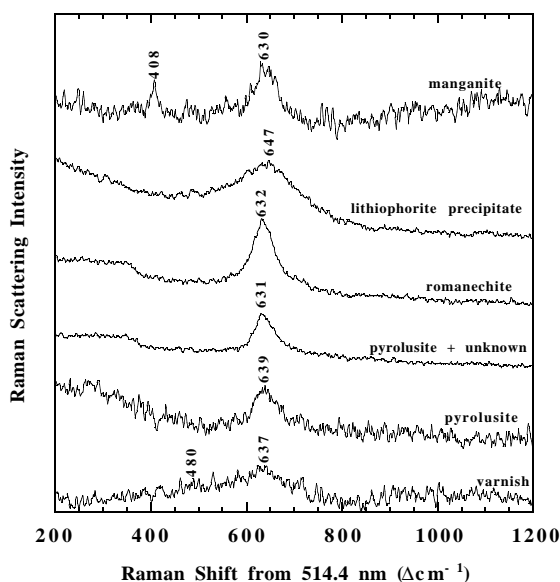


Figure 2: Raman spectra of the Mn-oxide standards used for comparison with the varnish spectra. A varnish spectrum is shown for comparison. The Mn-oxides are all characterized by peaks near 630 Δcm^{-1} , which is similar to peaks in many of the varnish spectra. The varnish peaks are all much broader, however, due to the overlap of bands in the ~400-700 Δcm^{-1} range (see bottom spectrum in Figure 3) and due to the fine-grained nature of the varnish. The broad band of the fine-grained lithiophorite precipitate suggests band broadening due to fine grain size.

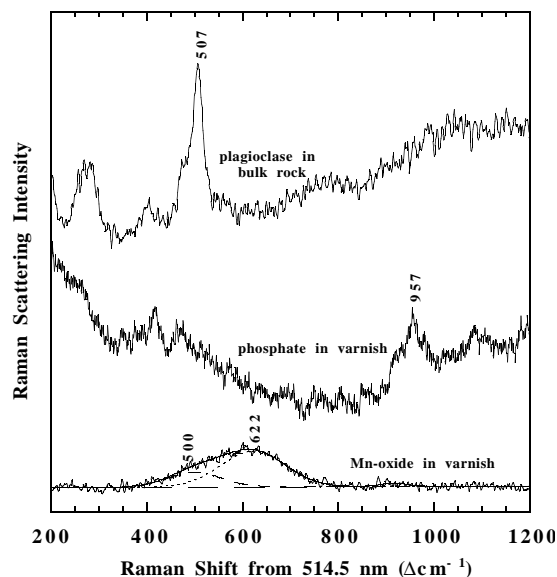


Figure 3: Raman spectra obtained directly from the varnish surface show that both the varnish and the bulk rock can be detected in this configuration. The top spectrum showing the characteristic main peak of plagioclase was taken from the unprepared surface of the hand sample at a location where the varnish is either absent or optically thin. The middle spectrum shows the main Ca-phosphate peak in the varnish coating. The bottom spectrum shows the broad Mn-oxide band common to many Raman spectra of this varnish. Curve fittings (dashed lines) suggest another broad band resulting from very fine-grained silicate phases which might exist in the varnish.